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# ONE-ELECTRON REDOX REACTIONS OF FREE RADICALS IN SOLUTION

## RATE OF ELECTRON TRANSFER PROCESSES TO QUINONES

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SUMMARY

A large number of biologically-important organic and inorganic free radicals have been produced in aqueous solutions, using the fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry. The reactions of these free radicals with menaquinone (vitamin $K_3$, $E_0 = 0.42$ V) were followed by observing the formation kinetics of the semiquinone radical anion of menaquinone, $\cdot MK^-$. The absorption spectrum of $\cdot MK^-$ has maxima at 395 nm and 300 nm, with extinction coefficients of $1.1 \cdot 10^4$ and $1.25 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$, respectively. The $pK_a$ of the radical $\cdot MK^- - H^+$ is $4.6 \pm 0.1$. The free radicals were produced by a one-electron oxidation or reduction of various compounds by hydroxyl radicals and solvated electrons, $e_{aq}^-$. Alcohols, sugars, carboxylic acids, amino acids, peptides, aliphatic amines and amides, aromatic and heterocyclic molecules, pyridine derivatives (nicotinamide, $NAD^+$), and transition metal ions have been examined. Significant differences have been observed in both the efficiency (expressed in percentage) and the rate constants of the electron transfer reactions from these free radicals to menaquinone. Absolute rates of electron transfer from approx. $5 \cdot 10^8$–$5 \cdot 10^9$ $M^{-1} \cdot s^{-1}$ have been observed for most of the free radicals studied. Information relating to the nature of the radicals and the acid–base properties of these radicals for effective one-electron redox reactions with quinones is indicated.

## INTRODUCTION

Many biological oxidation–reduction reactions have been shown to occur *via* the intermediary of free radicals (see, for example, Blois *et al.*[1] and King and Klingenberg[2]). While the presence of free radicals has been demonstrated by means of electron spin resonance spectroscopy and, in some cases, by absorption spectroscopy, very little kinetic information is available to show the reactivity of these free radicals, the nature of the reactions (oxidation or reduction) they undergo and the required properties of the substrates with which they react. These reactions are one-electron transfer reactions, and such electron transport systems have been shown to be necessary for phosphorylation, in mitochondrial and in several other enzymic oxidation reactions.

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In the presence of suitable electron donors or acceptors, electron transfer can occur effectively between the free radicals and the acceptor[3]. A large number of biologically-important organic and inorganic free radicals have been produced in this investigation, and the absolute values of the rate constants of these reactions have been determined in aqueous solutions using the fast-reaction technique of pulse radiolysis and kinetic absorption spectrophotometry. A quinone was chosen as the electron acceptor in this work since quinones have been used extensively as mediators in controlling the entry or reverse flow of electrons in biochemical reactions[2,4]. The function of quinones in biochemical electron transport systems is probably *via* the semiquinone radicals as active intermediates. Menaquinone (vitamin $K_3$) was selected due to its favorable redox potential, $E_0 = 0.42$ V, and its relative solubility in water.

## METHODS

The free radicals studied in this work were produced by reaction of substrates ($RH_2$) with either hydroxyl radicals or hydrated electrons, formed in the radiolysis of water

$$H_2O \xrightarrow{\wedge\wedge\wedge} OH, e_{aq}^-, H$$

with $G$-values (yield of free radicals per 100 eV of energy absorbed) of 2.75, 2.75 and 0.55, respectively. The radicals were generated according to Reactions 1 and 2:

$$OH + RH_2 \rightarrow {}^{\cdot}RH + H_2O \quad (1)$$

$$e_{aq}^- + RH_2 \rightarrow {}^{\cdot}RH_2^- \quad (2)$$

In order to examine separately the reactions of ${}^{\cdot}RH$ or ${}^{\cdot}RH_2^-$ produced from the solute ($RH_2$), the experiments were carried out (a) in aqueous solutions containing $N_2O$ (1 atm) in order to convert $e_{aq}^-$ to OH radicals

$$e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^- \quad (3)$$

where $k_3 = 5.6 \cdot 10^9$ $M^{-1} \cdot s^{-1}$ (Anbar and Neta[5]), or (b) in presence of 1.0 M *tert*-butanol to scavenge the OH radicals. The *tert*-butanol radical produced does not absorb above 280 nm and is relatively unreactive[6]. Furthermore, the results to be presented below were shown to be unaffected by the presence of the *tert*-butanol radicals in the solution. In this way, the free radicals were formed by a one-electron oxidation (using OH radicals) or reduction (using $e_{aq}^-$) of the substrate.

The rate constants of the redox reactions of the free radicals with menaquinone (MK) as the electron acceptor,

$${}^{\cdot}RH + MK \rightarrow {}^{\cdot}MK^- + R + H^+ \quad (4)$$

$${}^{\cdot}RH_2^- + MK \rightarrow {}^{\cdot}MK^- + RH_2 \quad (5)$$

were determined using the fast-reaction technique of pulse radiolysis. The experimental set-up used and the procedure have been described elsewhere[6–8]. Briefly, single pulses of approx. 30 ns duration of 2.3-MeV electrons were used and kinetic measure-

ments could be made with a time resolution of approx. 0.1 $\mu$s. In order to minimize the photolysis of menaquinone and of some of the solutes by the monitoring light from a 450-W Xenon lamp, appropriate cut-off filters as well as a synchronized electric shutter which opened for approx. 7–8 ms were used.

The rates of Reactions 4 and 5 were determined by observing the formation kinetics of $\cdot MK^-$ at 395 nm (see below), the absorption maximum of the semiquinone radical anion. The rates of formation were in all cases pseudo-first-order, dependent upon the concentration of MK. The concentration of MK was varied from $2 \cdot 10^{-5}$–$10 \cdot 10^{-5}$ M.

The chemicals used were the highest grade commercially available and were supplied by Calbiochem, Sigma, Cyclochemicals, Schwarz-Mann, Eastman, Baker and Mallinckrodt. Solutions were prepared immediately before carrying out the pulse radiolysis experiments, and the pH adjusted in an oxygen-free medium. $HClO_4$, KOH, phosphates (1–3 mM) and borates (1–3 mM) were used as buffers. Triply distilled water, further purified by radiolysis and photolysis, was used.

In Figs 1–5 given below, the spectra of the transient species were in all cases corrected for the depletion of menaquinone in the appropriate wavelength range where it absorbs light.

The efficiency, expressed in percentage, for the formation of the semiquinone radical of menaquinone from the reaction with various free radicals was determined, in each case, on the basis of the extinction coefficient of $\cdot MK^-$. This $\varepsilon$ was determined directly from the reaction with $e_{aq}^-$ (taken as 100% efficient, see below).

For the great majority of the systems studied the free radicals produced do not absorb at 400 nm. In the few cases where they do absorb their extinction coefficient was no more than approx. 15% that of $\cdot MK^-$.

## RESULTS AND DISCUSSION

Menaquinone (vitamin $K_3$, 2-methyl-1,4-naphthaquinone) was selected as the electron acceptor in this work, and the optical absorption spectra of the semiquinone radical and radical anions were determined directly by pulse radiolysis from the reaction with $e_{aq}^-$

$$e_{aq}^- + MK \rightarrow \cdot MK^- \tag{6}$$

$$\cdot MK^- + H^+ \rightleftharpoons \cdot MK^- - H^+ \tag{7}$$

where $k_6 = 5.4 \cdot 10^{10}$ $M^{-1} \cdot s^{-1}$. Numerous other semiquinones and ketyl radicals have been produced by this method[9,10]. Fig. 1 shows the transient spectra of $\cdot MK^-$ and $\cdot MK^- - H^+$ radicals. The spectrum of $\cdot MK^-$ has maxima at 395 nm and 300 nm and a shoulder at approx. 540 nm with extinction coefficients of $1.1 \cdot 10^4$ and $1.25 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$, respectively, and decays with $2k = 5.0 \cdot 10^8$ $M^{-1} \cdot s^{-1}$. The $\cdot MK^- - H^+$ radical has a maximum at 370 nm with $\varepsilon = 9.7 \cdot 10^3$ $M^{-1} \cdot cm^{-1}$, the second band could not be determined under these experimental conditions but was found[11] to have a $\lambda_{max} = 290$ nm and $\varepsilon = 6.0 \cdot 10^3$ $M^{-1} \cdot cm^{-1}$. The radical decays faster than the radical anion, with $2k = 3.0 \cdot 10^9$ $M^{-1} \cdot s^{-1}$. By monitoring the change in absorbance at 400 nm with pH, a "titration-type" curve is obtained (see insert Fig. 1) from which the $pK_a$ of the equilibrium of Reaction 7 was found to be $4.6 \pm 0.1$. These

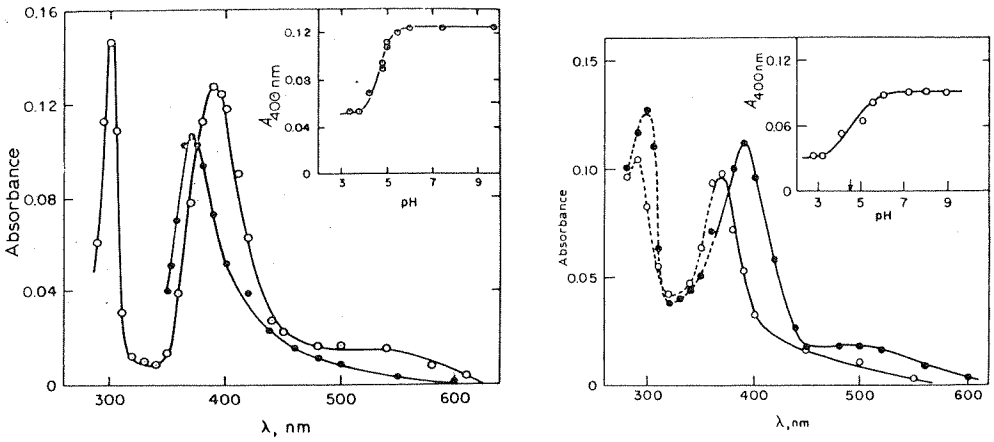


Fig. 1. Optical absorption spectra of the semiquinone radical of menaquinone, produced from the reaction of $e_{aq}^-$ with MK ($2 \cdot 10^{-4}$ M), in presence of 0.5 M *tert*-butanol, 1 atm Ar at pH 7.3 (⊙) and $5 \cdot 10^{-3}$ M MK, 2.0 M *tert*-butanol at pH 3.4 (●). Insert: absorbance at 400 nm *versus* pH.

Fig. 2. Transient optical absorption spectra produced from the reaction of OH radicals with MK ($2 \cdot 10^{-4}$ M, in presence of 1 atm $N_2O$), at pH 7.0 (●) and pH 3.2 (○). Insert: absorbance at 400 nm *versus* pH.

results are in good agreement with the parameters for these semiquinone radicals obtained[11] *via* Reaction 8:

$$(CH_3)_2\dot{C}OH + MK \rightarrow {}^{\bullet}MK^- + CH_3COCH_3 + H^+ \qquad (8)$$

Interestingly enough, the reaction of OH radicals with MK gives a rather similar transient absorption (Fig. 2) to that produced *via* $e_{aq}^-$, but with more intense "shoulders". The radical formed is presumably a semiquinone-type and has a $pK_a = 4.6 \pm 0.1$ (insert Fig. 2), similar to that produced *via* Reaction 6. The rate of formation of the radical on reaction with OH radicals was found to be $k = 5.1 \cdot 10^8$ $M^{-1} \cdot s^{-1}$, while the rate of OH radicals with MK as determined using the thiocyanate method[12] was found to be $7.9 \cdot 10^9$ $M^{-1} \cdot s^{-1}$. This difference in rates can be taken to mean that some of the OH radicals add to MK at positions which do not give rise to the semiquinone type of transient absorption.

*Reaction of radicals produced from alcohols and sugars*

Alcohols and sugars react with a high rate constant[5] with OH radicals by abstraction of a hydrogen atom, *e.g.* Reaction 9,

$$OH + RCH_2OH \rightarrow R\dot{C}HOH + H_2O \qquad (9)$$

Depending on the nature of the alcohol and the sugar, abstraction can take place at positions other than the α-position. The $R\dot{C}HOH$ radicals also undergo acid–base reactions

$$R\dot{C}HOH \rightleftharpoons R\dot{C}HO^- + H^+ \qquad (10)$$

TABLE I

EFFICIENCY AND RATE CONSTANTS OF ELECTRON TRANSFER FROM $R\dot{C}HOH$ AND $R\dot{C}HO^-$ RADICALS TO MENAQUINONE IN AQUEOUS SOLUTION

| *Alcohol* | *pH* | $pK_a$ (*radical*)* | *Donor radical*** | *% Transfer**** | *Rate* ($M^{-1}s^{-1}$)§ |
|---|---|---|---|---|---|
| Methanol | 7.0 | 10.7 | $\dot{C}H_2OH$ | 88.0 | $3.7 \cdot 10^9$ |
| | 12.4 | | $\dot{C}H_2O^-$ | 92.0 | $4.4 \cdot 10^9$ |
| Ethanol | 7.0 | 11.6 | $CH_3\dot{C}HOH$ | 90.0 | $3.8 \cdot 10^9$ |
| | 12.5 | | $CH_3\dot{C}HO^-$ | 92.0 | $4.2 \cdot 10^9$ |
| Isopropanol | 7.0 | 12.2 | $(CH_3)_2\dot{C}OH$ | 91.0 | $4.1 \cdot 10^9$ |
| | 12.4 | | $(CH_3)_2\dot{C}O^-$ | 91.0 | $4.2 \cdot 10^9$ |
| *n*-Butanol | 7.0 | | §§ | 32.3 | $4.1 \cdot 10^9$ |
| | 12.7 | — | | 40.0 | $4.2 \cdot 10^9$ |
| *tert*-Butanol | 7.0 | > 14§§§ | $\dot{C}H_2(CH_3)_2COH$ | ≤ 5.0 | — |
| | 12.4 | | $\dot{C}H_2(CH_3)_2COH$ | ≤ 5.0 | — |
| Ribose | 6.9 | — | $\cdot C_5H_9O_5$† | 60.0 | $1.4 \cdot 10^9$ |
| Deoxyribose | 6.8 | — | $\cdot C_5H_9O_4$† | 81.0 | $2.1 \cdot 10^9$ |
| Ascorbic acid | 3.3, 9.0 | — | †† | 43.0, 38.0 | ≈$1.3 \cdot 10^9$; $3.8 \cdot 10^9$ |

* From Asmus *et al.*[13].
** Produced from the reaction of OH radicals with $5 \cdot 10^{-2}$ M alcohols.
*** Values to ±5%.
§ Values to ±10%.
§§ Mixture of α- and β-hydroxyalkyl radicals.
§§§ From Simic *et al.*[6].
† From Simic and Hayon[22].
†† See text.

with $pK_a$ values of 10.7 and higher[6,13]. Table I gives the efficiency and rate constants for electron transfer of these radicals to menaquinone. The following points can be made: (i) the transfer of electrons from α-hydroxyalkyl radicals, $R\dot{C}HOH$, is quite efficient (⩾90%) whereas β- or γ-hydroxyalkyl radicals do not transfer to MK; (ii) the transfer from the radical anions $R\dot{C}HO^-$ is even more efficient (>90%); (iii) the radicals from deoxyribose at pH 6.8 are quite efficient in transfering an electron to MK, thus providing a mechanism for the formation of a keto sugar, based on a reaction similar to Reaction 8; (iv) the radicals produced from ascorbic acid[14–16] have not been clearly identified, and the low efficiency of transfer (approx. 40%) to MK would appear to indicate the formation of more than one radical from ascorbic acid; (v) the rates of electron transfer to MK are all close to approx. $4.0 \cdot 10^9\ M^{-1} \cdot s^{-1}$.

*Reaction of radicals produced from aliphatic acids*

The reactions of OH radicals with monobasic and dibasic aliphatic carboxylic acids have been studied recently[17,18], and the effect of substituted functional groups examined. The following reactions have been suggested:

$$OH + RCH_2COOH \rightarrow R\dot{C}HCOOH + H_2O \quad (11)$$

$$R\dot{C}HCOOH \rightleftharpoons R\dot{C}HCOO^- + H^+ \quad (12)$$

where R=H or $CH_3$. When R=OH, *e.g.* glycolic acid, the radical undergoes additional acid–base reactions:

$$OH + OHCH_2COOH \rightarrow OH\dot{C}HCOOH + H_2O \quad (13)$$

$$OH\dot{C}HCOOH \rightleftharpoons OH\dot{C}HCOO^- + H^+ \quad (14)$$

$$OH\dot{C}HCOO^- \rightleftharpoons {}^-O\dot{C}HCOO^- + H^+ \quad (15)$$

and $pK_a$ values of 4.8 and 8.8 have been obtained for Equilibria 14 and 15, respectively.

Table II presents the percentage and rates of electron transfer from various radicals to MK. The following points can be made: (i) hydroxyl radicals react with formic acid to produce $\cdot CO_2^-$ radicals and these transfer to MK with approx. 100% efficiency, and $k_{17} = 4.8 \cdot 10^9\ M^{-1} \cdot s^{-1}$

$$OH + HCO_2^- \rightarrow \cdot CO_2^- + H_2O \quad (16)$$

$$\cdot CO_2^- + MK \rightarrow \cdot MK^- + CO_2 \quad (17)$$

(ii) the radicals $R\dot{C}HCOOH$ and $R\dot{C}HCOO^-$ (where R=H, $CH_3$, $C_2H_5$) essentially do not transfer to MK; (iii) radicals from monobasic acids with α-hydroxyl groups, such as glycolic and lactic acids, do transfer and the efficiency of electron transfer increases on deprotonation of both the carboxyl and hydroxyl groups of the radicals

TABLE II

EFFICIENCY AND RATE CONSTANTS OF ELECTRON TRANSFER FROM FREE RADICALS PRODUCED FROM ALIPHATIC ACIDS TO MENAQUINONE IN AQUEOUS SOLUTION

| *Aliphatic acid* | *pH* | $pK_a$ (*radical*) | *Donor radical* | *% Transfer** | *Rate* $(M^{-1} \cdot s^{-1})$** |
|---|---|---|---|---|---|
| Formic acid | 6.9 | 3.9 | $CO_2^{-}$*** | ≈100 | $4.8 \cdot 10^9$ |
| Acetic acid | 3.2–10.8 | 4.5 | $\dot{C}H_2COOH$, $\dot{C}H_2COO^-$*** | ≈ 9.0 | — |
| Propionic acid | 3.2–12.4 | 4.9 | $CH_3\dot{C}HCOOH$, $CH_3\dot{C}HCOO^-$*** | ≈ 7.0 | — |
| *n*-Butyric acid | 6.5–12.4 | 4.8 | $CH_3CH_2\dot{C}HCOO^-$*** | ≈ 15.0 | — |
| *i*-Butyric acid | 6.0 | 5.8 | $(CH_3)_2\dot{C}COO^-$*** | ≈ 4.0 | — |
| Pivalic acid | 11.0 | 4.8 | $\dot{C}H_2C(CH_3)_2COO^-$*** | ≈ 6.0 | — |
| Glycolic acid | 3.2 | | $HO\dot{C}HCOOH$§ | 13.0 | $9.2 \cdot 10^8$ |
| | 6.5 | 4.8 | $HO\dot{C}HCOO^-$§ | 69.0 | $1.5 \cdot 10^9$ |
| | 10.6 | 8.8 | $^-O\dot{C}HCOO^-$ | 77.0 | $1.6 \cdot 10^9$ |
| Lactic acid | 3.2 | | $HO\dot{C}(CH_3)COOH$§ | 15.0 | — |
| | 6.5 | 5.3 | $HO\dot{C}(CH_3)COO^-$§ | 55.0 | $1.4 \cdot 10^9$ |
| | 10.6 | 9.8 | $^-O\dot{C}(CH_3)COO^-$§ | 72.0 | $1.9 \cdot 10^9$ |
| Methyl lactate | 3.2 | | $HO\dot{C}(CH_3)COOCH_3$ | 20.0 | — |
| | 10.4 | — | $^-O\dot{C}(CH_3)COOCH_3$ | 74.0 | $2.3 \cdot 10^9$ |
| Malonic acid | 4.5 | 5.7 | $HOOC\dot{C}HCOOH$§ | ≈ 7.0 | — |
| | 10.8 | | $^-OOC\dot{C}HCOO^-$§ | ≈ 9.0 | — |
| Succinic acid | 9.2 | — | $^-OOC\dot{C}HCH_2COO^-$§ | ≈ 6.0 | — |
| Malic acid | 7.0 | — | $^-OOC\dot{C}(OH)CH_2COO^-$ | 47.0 | $1.1 \cdot 10^9$ |
| Glutaric acid | 6.4, 10.9 | — | $^-OOCCH_2\dot{C}H_2CHCOO^-$ | ≈ 4.0 | — |
| Tartaric acid | 3.2 | 4.5 | $HOOCCH(OH)\dot{C}(OH)COOH$§ | 14.0 | $7.0 \cdot 10^8$ |
| | 11.0 | | $^-OOCH(OH)\dot{C}(OH)COO^-$§ | 69.0 | $7.0 \cdot 10^8$ |
| Citric acid | 3.2, 10.4 | — | | ≈ 12.0 | — |
| Maleic acid, fumaric acid | 7.2 | — | $^-OOCCH(OH)\dot{C}HCOO^-$ | ≈ 11.0 | — |

* Values to ±5%.
** Values to ±10%.
*** From Neta *et al.*[17].
§ From Simic *et al.*[18].

$R\dot{C}(OH)COOH < R\dot{C}(OH)COO^- < R\dot{C}(O^-)COO^-$; the following reactions are suggested

$$R\dot{C}(OH)COO^- + MK \rightarrow RCOCOO^- + {}^{\cdot}MK^- + H^+ \quad (18)$$

$$R\dot{C}(O^-)COO^- + MK \rightarrow RCOCOO^- + {}^{\cdot}MK^- \quad (19)$$

(iv) similar results are obtained with dibasic acids. The radicals from malonic, succinic and glutaric acids essentially do not transfer, whereas the radicals from malic and tartaric acids do transfer to MK. The efficiency of the latter radicals also increases on deprotonation of both the carboxyl and hydroxyl groups; (v) the addition of OH radicals to unsaturated acids, *e.g.* maleic and fumaric acids, produces $\beta$-radicals with respect to the hydroxyl group. Such $\beta$-radicals do not transfer (see alcohols above) and essentially no transfer was found (Table II).

*Reaction of radicals produced from amino acids and peptides*

The sites of attack by oxidizing radicals on aliphatic amino acids and peptides are markedly dependent upon the state of protonation of the various functional groups[19,20] (Rao, P. S. and Hayon, E., unpublished results), *e.g.*

$$OH + \overset{+}{N}H_3CH_2CONHCH_2COOH \rightarrow \overset{+}{N}H_3CH_2CONHC\dot{H}COOH + H_2O \quad (20)$$

$$\overset{+}{N}H_3CH_2CONHC\dot{H}COOH \underset{pK_a \text{ approx. } 5.0}{\rightleftharpoons} \overset{+}{N}H_3CH_2CONHC\dot{H}COO^- + H^+ \quad (21)$$

$$OH + NH_2CH_2CONHCH_2COO^- \rightarrow NH_2\dot{C}HCONHCH_2COO^- + H_2O \quad (22)$$

$$NH_2\dot{C}HCONHCH_2COO^- \underset{pK_a > 12.6}{\rightleftharpoons} \overset{-}{N}H\dot{C}HCONHCH_2COO^- + H^+ \quad (23)$$

The deprotonation of the peptide hydrogen adjacent to the unpaired electron was established for glycine anhydride[21]:

$$\underline{NH\dot{C}HCONHCH_2CO} + OH^- \rightleftharpoons {}^-\underline{N\dot{C}HCONHCH_2CO} + H_2O \quad (24)$$

with $k_{24} = 8.0 \cdot 10^9 \pm 2.0 \cdot 10^9$ $M^{-1} \cdot s^{-1}$ and $pK_a = 9.6$. A reaction similar to Reaction 24 was found not to occur for the sarcosine anhydride radical $\underline{N(CH_3)\dot{C}HCON(CH_3)CH_2CO}$.

The efficiency and the rate constants for the formation of ${}^{\cdot}MK^-$ from these radicals are given in Table III. The $NH_2\dot{C}HCOOH$ radical transfers 71% whereas the $\overset{+}{N}H_3\dot{C}HCONH_2$ radical transfers only 24%. Electron transfer from a radical with an $\alpha$-amino group was suggested[11,22] to occur according to Reaction 25

$$NH_2\dot{C}HCOOH + MK \rightarrow NHCHCOOH + {}^{\cdot}MK^- + H^+ \quad (25a)$$

$$NH_2\dot{C}HCOO^- + MK \rightarrow NHCHCOO^- + {}^{\cdot}MK^- \quad (25b)$$

TABLE III

EFFICIENCY AND RATE CONSTANTS OF ELECTRON TRANSFER FROM AMINO ACIDS AND PEPTIDE FREE RADICALS TO MENAQUINONE IN AQUEOUS SOLUTION

| *Solute* | *pH* | $pK_a$ (*radical*) | *Donor radical* | *% Transfer** | *Rate* $(M^{-1} \cdot s^{-1})$** |
|---|---|---|---|---|---|
| Glycine | 5.4 | ≈ 6.4 | $NH_3\dot{C}HCOO^-$*** | 71.0 | $5.5 \cdot 10^9$ |
| | 8.0 | | $NH_2\dot{C}HCOO^-$ | 79.0 | $4.0 \cdot 10^9$ |
| Glycine amide | 3.2 | 4.3 | $\overset{+}{N}H_3\dot{C}HCONH_2$§ | 24.0 | $3.6 \cdot 10^9$ |
| | 10.4 | | $NH_2\dot{C}HCONH_2$ | 41.0 | $5.4 \cdot 10^9$ |
| Sarcosine | 6.0 | — | $NH(CH_3)\dot{C}HCOO^-$ | 33.0 | $1.1 \cdot 10^9$ |
| | 12.5 | | $\bar{N}(CH_3)\dot{C}HCOO^-$ | 64.0 | $1.7 \cdot 10^9$ |
| Glycylglycine | 6.6 | 5.0 | $\overset{+}{H}_2$–Gly–$NH\dot{C}HCOO^-$§§ | 19.0 | — |
| | 11.0 | | $NH_2\dot{C}HCO$–Gly–$O^-$ | 47.0 | $1.2 \cdot 10^9$ |
| Glycylglycine amide | 5.5 | ≈ 6.7 | $\overset{+}{H}_2$–Gly–$NH\dot{C}HCONH_2$§ | 16.0 | — |
| | 6.8 | | | 25.0 | $8.5 \cdot 10^8$ |
| | 11.0 | | $NH_2\dot{C}HCO$–Gly–$NH_2$ | 45.0 | $8.5 \cdot 10^8$ |
| Glycylsarcosine | 6.8 | | $\overset{+}{H}_2$–Gly–$N(CH_3)\dot{C}HCOO^-$§ | 20.0 | — |
| | 10.9 | | $NH_2\dot{C}HCO$–Sar–$O^-$ | 46.0 | $1.0 \cdot 10^9$ |
| Triglycine | | ≈ 5.0 | $\overset{+}{H}_2$–Gly–Gly–$NH\dot{C}HCOOH$§§ | | |
| | 7.0 | | $\overset{+}{H}_2$–Gly–Gly–$NH\dot{C}HCOO^-$ | 11.0 | $1.8 \cdot 10^9$ |
| | 12.0 | ≈13.3 | $NH_2\dot{C}HCO$–Gly–Gly–$O^-$§§§ | 77.0 | $1.8 \cdot 10^9$ |
| Acetylsarcosine | 7.0 | — | $CH_3CON(CH_3)\dot{C}HCOO^-$ | 39.0 | $1.3 \cdot 10^9$ |
| | 12.5 | — | $CH_3CON(CH_3)\dot{C}HCOO^-$ | 38.0 | $1.0 \cdot 10^9$ |
| Acetyldiglycine | 6.8 | 4.5 | Ac–Gly–$NH\dot{C}HCOO^-$§§ | 4.0 | — |
| | 12.3 | | | 55.0 | $3.8 \cdot 10^9$ |
| Acetyltriglycine | 6.0 | | Ac–Gly–Gly–$NH\dot{C}HCOO^-$§ | 11.0 | — |
| | 12.5 | 11.5 | Ac–Gly–Gly–$\bar{N}\dot{C}HCOO^-$ | 50.0 | $3.7 \cdot 10^9$ |

TABLE III (*continued*)

| *Solute* | *pH* | $pK_a$ (*radical*) | *Donor radical* | *% Transfer** | *Rate* $(M^{-1} \cdot s^{-1})^{**}$ |
|---|---|---|---|---|---|
| Acetyltrialanine | 6.9 | | Ac–Ala–Ala–$NH\dot{C}(CH_3)COO^-$§ | 18.0 | $2.1 \cdot 10^9$ |
| | 12.3 | 10.9 | Ac–Ala–Ala–$\bar{N}\dot{C}(CH_3)COO^-$ | 47.0 | $2.6 \cdot 10^9$ |
| Aectyltrisarcosine | 7.0 | — | Ac–Sar–Sar–$N(CH_3)\dot{C}HCOO^-$§ | 39.0 | |
| | 12.5 | | | | |
| Acetylserine amide | 6.0 | | Ac–Sar–Sar–$N(CH_3)\dot{C}HCOO^-$ †† | 39.0 | $1.3 \cdot 10^9$ |
| | 9.0 | | | 52.0 | $1.5 \cdot 10^9$ |
| | 11.0 | | | 57.0 | $1.5 \cdot 10^9$ |
| Acetylasparagine | 3.2, 6.0 | | †† | 68.0 | $1.9 \cdot 10^9$ |
| | 11.0 | | | ≈12.0 | — |
| | 12.5 | | | | |
| Glycine anhydride | 6.9 | 9.6 | $\underline{NH\dot{C}HCONHCH_2CO}$† | 39.0 | $1.5 \cdot 10^9$ |
| | 10.9 | | $\underline{\bar{N}\dot{C}HCONHCH_2CO}$ | Nil | — |
| Alanine anhydride | 6.9 | 9.6 | $\underline{NH\dot{C}(CH_3)CONHCH(CH_3)CO}$† | 88.0 | $4.0 \cdot 10^9$ |
| | 10.9 | | $\underline{\bar{N}\dot{C}(CH_3)CONHCH(CH_3)CO}$ | ≈ 4.0 | — |
| Sarcosine anhydride | 6.9, 10.9 | — | $\underline{N(CH_3)\dot{C}HCON(CH_3)CH_2CO}$† | 75.0 | $3.1 \cdot 10^9$ |
| | | | | ≈ 2.0 | — |

* Values to ±5%.
** Values to ±10%.
*** From Neta *et al.*[19].
§ From Rao and Hayon, unpublished.
§§ From Simic *et al.*[20].
§§§ Mixture of radicals, see Simic *et al.*[20].
† From Hayon and Simic[21].
†† Radical uncertain.

It follows, therefore, that the efficiency of electron transfer from a protonated α-amino group (*e.g.* $\overset{+}{N}H_3\dot{C}HCONH_2$) should be considerably lower. The low electron transfer from $\overset{+}{N}H_3CH_2CONH\dot{C}HCOO^-$ probably gives $\cdot MK^-$ and $\overset{+}{N}H_3CH_2$-CONCHCOO$^-$. The behavior of an α-amino radical in this general mechanism is to transfer an electron effectively when it is in the $NH_2\dot{C}H$ form or the $\overline{N}H\dot{C}H$ form, but not in the $\overset{+}{N}H_3\dot{C}H$ form. In support of this mechanism, the deprotonated radicals from glycine and alanine anhydrides transfer efficiently to MK, whereas the sarcosine anhydride radical does not (Table III).

Fig. 3 shows the transient absorption spectra observed on pulse radiolysis of glycine anhydride with MK at pH 10.8. At 0.2 μs after the pulse one observes part (the rest is masked by the absorption of MK) of the spectrum of the $\overline{N}\dot{C}HCONHCH_2CO$ radical in agreement with earlier results[21]; at 40 μs after the pulse, maximum electron transfer occurs and one observes a transient similar to that of $\cdot MK^-$ and with an

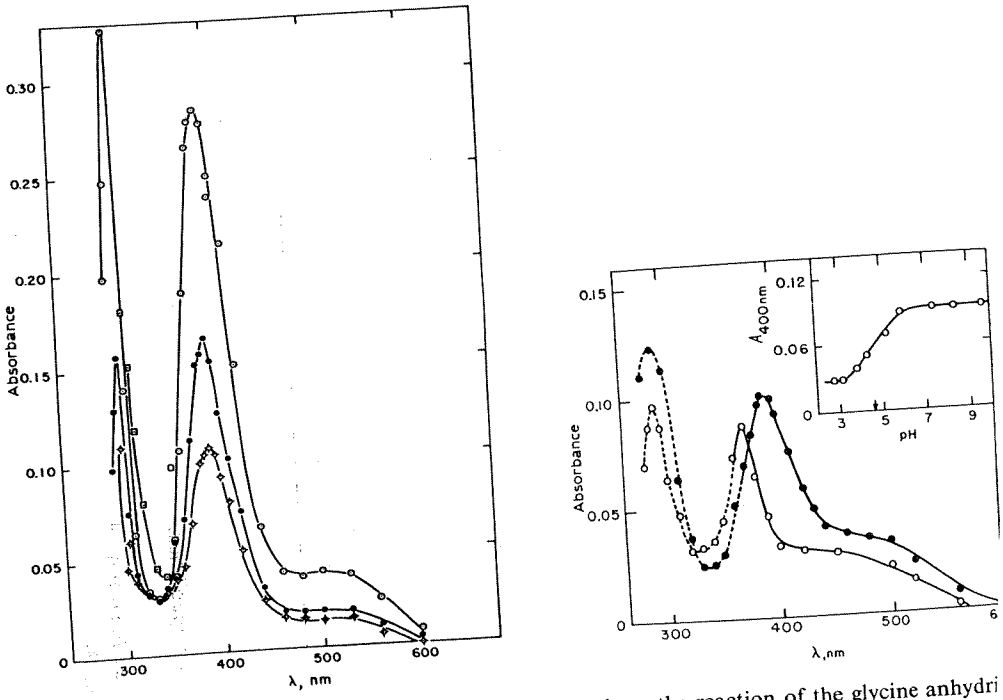


Fig. 3. Transient optical absorption spectra produced from the reaction of the glycine anhydri radicals $\overline{N}\dot{C}HCONHCH_2CO$ with MK ($5 \cdot 10^{-5}$ M MK, $5 \cdot 10^{-3}$ M glycine anhydride, 1 atm $N_2$ at pH 10.8. Absorbance read at 0.2 μs (⊡), 40 μs (⊙), 700 μs (●) and 1 min. (-⊙-) after electr pulse.

Fig. 4. Transient absorption spectra produced from the reaction of $CH_3CON(CH_3)\dot{C}HCO$ radicals with MK ($1 \cdot 10^{-4}$ M MK, $1 \cdot 10^{-2}$ M *N*-acetylsarcosine, 1 atm $N_2O$) at pH 7.0 (●) pH 3.2 (⊙). Insert: absorbance at 400 nm *versus* pH.

TABLE IV

EFFICIENCY AND RATE CONSTANTS OF ELECTRON TRANSFER FROM ALIPHATIC AMINES AND AMIDES TO MENAQUINONE IN AQUEOUS SOLUTION

| *Solute* | *pH* | $pK_a$ (*radical*) | *Donor radical** | *% Transfer*** | *Rate* $(M^{-1} \cdot s^{-1})$*** |
|---|---|---|---|---|---|
| Ethylamine | 7.5 | ≈ 5.5 | $\dot{C}H_2CH_2NH_2$ § | 10.0 | — |
| | 11.6 | ≈10.4 | $CH_3\dot{C}HNH_2$ or $CH_3CH_2\dot{N}H$ | 34.0 | $3.3 \cdot 10^9$ |
| Isopropylamine | 9.0 | 6.0 | § | 14.0 | — |
| | 11.4 | 10.7 | $(CH_3)_2\dot{C}NH_2$ § | 41.0 | $3.6 \cdot 10^9$ |
| Triethylamine | 8.0 | 6.0 | § | ≈10.0 | — |
| | 11.6 | 9.5 | § | 37.0 | $4.6 \cdot 10^9$ |
| Acetamide | 6.0, 10.9 | — | $\dot{C}H_2CONH_2$, $CH_3\dot{C}ONH$ §§ | ≈17.0 | $1.1 \cdot 10^9$ |
| *N*-Methylacetamide | 6.0, 10.9 | — | $CH_3CONH\dot{C}H_2$ §§ | 19.0 | $2.0 \cdot 10^9$ |
| *N,N*-Dimethylacetamide | 6.0, 10.9 | — | $CH_3CON(\dot{C}H_2)CH_3$ §§ | 11.0 | — |
| Glycolamide | 7.1 | 5.5 | $H\dot{C}(O^-)CONH_2$ | 48.0 | $2.3 \cdot 10^9$ |

* Suggested radical.

** Values to ±5%.

*** Values to ±10%.

§ From Simic *et al.*[23].

§§ From Hayon *et al.*[12].

identical extinction coefficient; the semiquinone radical anion decays to give (in this case only) a permanent product with a spectrum similar to that of $\cdot MK^-$.

The radicals from *N*-acetylsarcosine and *N*-acetyltrisarcosine were found to produce $\cdot MK^-$ with approx. 35–40% efficiency. Fig. 4 shows the transient spectra produced from the reaction of *N*-acetylsarcosine with MK. These spectra and the $pK_a$ are closely similar to those produced from the reaction of $e_{aq}^-$ with MK (Fig. 1). No explanation is presently available to account for the observed transfer of electrons from these radicals (these radicals might be adding to MK or the peptides are impure).

*Reaction of radicals produced from aliphatic amines and amides*

Hydroxyl radicals react with aliphatic amines to give intermediates which undergo acid–base reactions[23]. The exact nature of these radicals has not been established. However, reaction with MK occurs (see Table IV) when the amino group is in an α-position to the odd electron and when it is not present in the $\overset{+}{N}H_3\dot{C}H$ form.

The sites of attack of OH radicals on amides are well characterized[12]. Very little transfer occurs (Table IV). The greater (albeit quite small) amount of transfer from the $CH_3CONH\dot{C}H_2$ radical compared to $CH_3CON(\dot{C}H_2)CH_3$ is probably due to the availability of an amide hydrogen. The radical from glycolamide transfers more efficiently because of the presence of ionized functional groups.

*Reaction of radicals produced from aromatic and heterocyclic compounds*

Hydroxyl radicals normally add to unsaturated aromatic and heterocyclic compounds. The OH-adducts produced transfer some 20–40% to MK, see Table V

TABLE V

EFFICIENCY AND RATE CONSTANTS OF ELECTRON TRANSFER FROM FREE RADICALS OF AROMATIC AND HETEROCYCLIC COMPOUNDS TO MENAQUINONE IN AQUEOUS SOLUTION

| *Solute* | *pH* | *Donor radical* | *% Transfer** | *Rate* $(M^{-1} \cdot s^{-1})$** |
|---|---|---|---|---|
| Phenol | 3.0 | OH radical adduct | 34.0 | $3.8 \cdot 10^9$ |
| | 5.8, 7.1 | | 39.0–44.0 | $3.3 \cdot 10^9$ |
| Tyrosine | 7.7, 9.1, 11.2 | | 32.0–37.0 | $\approx 4.0 \cdot 10^9$ |
| Phenylalanine | 6.8, 9.2 | | ≈ 5.0 | — |
| Tryptophan | 6.8 | | ≈20.0 | $2.8 \cdot 10^9$ |
| Indole | 7.0 | | ≈20.0 | $2.9 \cdot 10^9$ |
| Aniline | 7.0, 10.9 | | 26.0 | $4.0 \cdot 10^9$ |
| Nicotinamide | 6.8 | | 12.0 | — |
| | 11.4 | | 20.0 | $\approx 2.9 \cdot 10^9$ |
| *N'*-Methylnicotinamide | 7.0 | | 20.0 | $2.7 \cdot 10^9$ |
| | 10.9 | | 35.0 | $3.0 \cdot 10^9$ |
| *N,N*-Diethylnicotinamide | 7.1, 11.1 | | 27.0, 30.0 | $2.8 \cdot 10^9$ |
| Imidazole | 6.9 | | 84.0 | $1.6 \cdot 10^9$ |
| Histidine | 6.9 | | 88.0 | $1.2 \cdot 10^9$ |

* Values to ±5%.
** Values to ±10%.

In most of these cases, the odd electron is in a $\beta$-position to the OH group. Such a radical was shown above not to transfer to MK. Addition of OH to phenol and tyrosine produces phenoxyl radicals RO· (Land and Ebert[24], Feitelson and Hayon[25]). The subsequent reactions with MK are not clear. It is interesting to point out that some of the OH-adducts of pyrimidine bases do react effectively with MK, and the efficiency of electron transfer was found to depend on the pyrimidine base itself and on the various tautomeric forms of the radicals[11]. Similarly, the OH-adducts to imidazole and histidine transfer effectively to MK (Table V). In these cases, the heterocyclic nitrogen is probably involved in the electron transfer.

*Reaction of radicals produced by addition of $e_{aq}^-$ to various organic compounds*

Hydrated electrons are reactive species and interact with various molecules, usually (a) by addition, to give radical anions which may protonate (depending on the pH of the experiment and the $pK_a$ of the radical) to give the radical, or (b) the molecule undergoes dissociative electron capture to form a radical unrelated to that of the parent compound, *e.g.* $e_{aq}^- + RCl \rightarrow [RCl^-] \rightarrow R\cdot + Cl^-$.

Radicals produced by Method a above were made to react with MK (see Table VI), and in almost all cases the percentage of electron transfer was >90% and the rate approx. $4 \cdot 10^9$–$5 \cdot 10^9$ $M^{-1} \cdot s^{-1}$. Electrons add to ketocarboxylic acids (*e.g.* acetoacetic acid, α-ketoglutaric acid) to produce the corresponding α-alcohol radical:

$$e_{aq}^- + RCOCOO^- \rightarrow R\dot{C}(O^-)COO^- \quad (26)$$

$$R\dot{C}(O^-)COO^- + H^+ \rightleftharpoons R\dot{C}(OH)COO^- \quad (27)$$

$$R\dot{C}(OH)COO^- + MK \rightarrow RCOCOO^- + \cdot MK^- + H^+ \quad (28)$$

Similarly, $e_{aq}^-$ add to nicotinamide, $NAD^+$ and other related pyridine compounds, presumably at the ring[26] (Bruhlmann, U. and Hayon, E., unpublished results) and protonate rapidly to produce pyridinyl radicals. These latter radicals are found to transfer with a high rate constant to MK, Table VI. The considerable increase in the efficiency of transfer of the electron adducts of $Phe\text{–}NH_2 < Tyr\text{–}NH_2 < Try\text{–}NH_2$ is most interesting (Table VI) and suggests that the electrons add to the ring in $Tyr\text{–}NH_2$ and $Try\text{–}NH_2$ but not in $Phe\text{–}NH_2$. These conclusions are in agreement with other results[25] (Mittal and Hayon, E., unpublished work). The efficient transfer from imidazole and histidine (Table IV) again suggests addition of $e_{aq}^-$ to the ring and electron transfer from the cyclic nitrogen.

Addition of electrons to peptide linkages (*e.g.* dicyclic anhydrides) produces short-lived intermediates[21] which transfer effectively to MK.

$$-\dot{C}(OH)NH- + MK \rightarrow -COHN- + \cdot MK^- + H^+ \quad (29)$$

Since sarcosine derivatives $-CON(CH_3)-$ transfer as well and as fast as $-CONH-$ derivatives, it follows that the peptide hydrogen is not involved in these reactions.

TABLE VI

EFFICIENCY AND RATE CONSTANTS OF ELECTRON TRANSFER FROM ELECTRON ADDUCTS TO MENAQUINONE IN AQUEOUS SOLUTION

| *Solute* | *pH* | *Donor radical** | *% Transfer*** | *Rate* $(M^{-1} \cdot s^{-1})$*** |
|---|---|---|---|---|
| Ketomalonic acid | 9.2 | $-O-\dot{C}-(-COO^-)_2$ | 94.0 | $2.5 \cdot 10^9$ |
| Oxaloacetic acid | 6.2 | $-OOCCH_2\dot{C}(OH)COO^-$ | 92.0 | $3.1 \cdot 10^9$ |
| Acetoacetic acid | 9.2 | $CH_3\dot{C}(O^-)CH_2COO^-$ | 95.0 | $3.7 \cdot 10^9$ |
| α-Ketoglutaric acid | 10.2 | $-OOC(CH_2)_2-\dot{C}(O^-)COO^-$ | 94.0 | $3.8 \cdot 10^9$ |
| Nicotinamide | 7, 10.9 | § | 97.0 | $5.1 \cdot 10^9$ |
| *N'*-Methyl nicotinamide | 6.8, 10.9 | § | 99.0 | $4.9 \cdot 10^9$ |
| Diethyl nicotinamide | 7.0 | § | 99.0 | $4.1 \cdot 10^9$ |
| Nicotinic acid | 6.5 | § | 99.0 | $4.4 \cdot 10^9$ |
| $NAD^+$ | 6.2 | NAD·§ | 99.0 | $3.1 \cdot 10^9$ |
| Glycine anhydride | 6.9 | $NHCH_2\dot{C}(OH)NHCH_2CO$§§ | 98.0 | $4.9 \cdot 10^9$ |
| Alanine anhydride | 6.0 | $NHCH(CH_3)\dot{C}(OH)NHCH(CH_3)CO$§§ | 92.0 | $4.8 \cdot 10^9$ |
| Sarcosine anhydride | 6.0 | $N(CH_3)CH_2\dot{C}(OH)N(CH_3)CH_2CO$§§ | 91.0 | $4.6 \cdot 10^9$ |
| Acetyl glycylglycine amide | 7.0 | — | 99.0 | $2.7 \cdot 10^9$ |
| Phenylalanine amide | 6.0 | — | < 10.0 | — |
| Tyrosine amide | 6.0 | — | 38.0 | $1.5 \cdot 10^9$ |
| Tryptophan amide | 6.0 | — | 70.0 | $2.0 \cdot 10^9$ |
| Imidazole | 6.9 | — | 98.0 | $1.2 \cdot 10^9$ |
| Histidine | 6.9 | — | 97.0 | $1.2 \cdot 10^9$ |

* Produced by reaction of $e_{aq}^-$ with solute, in presence of 1.0 M *tert*-butanol to scavenge OH radicals; nature of radical $-\dot{C}-$ (OH) or $-\dot{C}-$ ($O^-$) is not known for certain in some cases.

** Values to ±5%.

*** Values to ±10%.

§ Electron presumably adds to the pyridine ring and is rapidly protonated (Brühlmann, U. and Hayon, E., unpublished results).

§§ From Hayon and Simic[21].

*Reactions of odd-valent inorganic radicals*

Divalent transition metal ions react with $e_{aq}^-$ very fast[5] and the products of this reaction are monovalent ions in their ground state.

$$M^{2+} + e_{aq}^- \rightarrow M^{+\cdot} \tag{30}$$

The formation of $Co^+$, $Ni^+$, $Zn^+$, $Cd^+$ have been demonstrated by pulse radiolysis[27]. The chemical behavior of these unique reduced species with MK has been studied, see Table VII. The monovalent ions react with MK very efficiently, approx. 90–100% transfer, and with high rates of electron transfer:

$$M^+ + MK \rightarrow M^{2+} + {}^{\cdot}MK^- \tag{31}$$

Fig. 5 shows the transient spectra of the radicals produced from the reaction of $Co^+$ with MK. The absorption spectra and the $pK_a$ of the radical (insert Fig. 5) are in excellent agreement with the radicals $^{\cdot}MK^-$ and $^{\cdot}MK^- - H^+$ produced from reaction with $e_{aq}^-$.

TABLE VII

EFFICIENCY AND RATE CONSTANTS OF ELECTRON TRANSFER FROM ODD-VALENT INORGANIC SPECIES TO MENAQUINONE IN AQUEOUS SOLUTION

| *Inorganic ions* | *pH* | *Donor radical** | *% Transfer*** | *Rate* $(M^{-1} \cdot s^{-1})$*** |
|---|---|---|---|---|
| Cobalt sulfate | 7.3 | $Co^+$ | 99.0 | $4.0 \cdot 10^9$ |
| Nickel sulfate | 7.0 | $Ni^+$ | 95.0 | $2.5 \cdot 10^9$ |
| Lead perchlorate | 7.2 | $Pb^+$ | 94.8 | $3.7 \cdot 10^9$ |
| Zinc sulfate | 7.1 | $Zn^+$ | 97.3 | $3.8 \cdot 10^9$ |
| Cadmium sulfate | 7.0 | $Cd^+$ | 99.0 | $4.6 \cdot 10^9$ |
| Silver sulfate | 7.0 | $Ag^\circ$ | 24.0 | — |
| Copper sulfate | 8.0 | § | 20.3 | — |
| | 10.6 | § | 39.0 | — |
| Cupric perchlorate | 9.0, 10.6 | § | 40.0 | $2.0 \cdot 10^9$ |
| Thallous sulfate | 6.8 | $Tl^{2+}$§ | 14.0 | — |
| Potassium iodide | 7.0 | $I_2^-$§ | Nil | — |
| Potassium bromide | 7.0 | $Br_2^-$§ | Nil | — |
| Sodium carbonate | 11.8 | $CO_3^-$§ | Nil | — |
| Hydrazine sulfate | 7.8, 11.2 | $\dot{N}_2H_3$§ | Nil | — |
| Hydroxylamine | 7.0 | $\dot{N}HOH$§ | Nil | — |

* Produced from the reaction of $e_{aq}^-$ with $5 \cdot 10^{-3}$ M inorganic ions.
** Values to ±5%.
*** Values to ±10%.
§ Produced from reaction with OH radicals.

Many biological oxidation–reduction reactions require metal ions. Reactions similar to Reaction 31 might also be of some importance in the redox reactions of metalloenzymes (*e.g.* cytochrome, vitamin B12 *etc.*).

The odd valent ions of silver and copper do not appear to react as effectively. The efficiency of electron transfer appears to be dependent upon the pH and upon

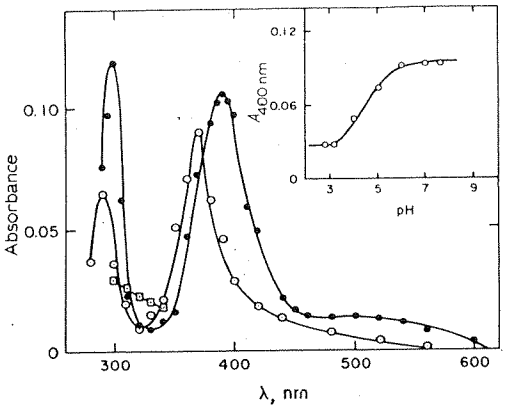


Fig. 5. Transient absorption spectra produced from the reaction of $Co^+$ radicals with MK ($5 \cdot 10^{-5}$ M MK, $5 \cdot 10^{-3}$ M $CoSO_4$, 0.5 M *tert*-butanol, 1 atm Ar), at pH 7.3 (●) and pH 3.2 (⊙). Partial absorption spectrum of $Co^+$ shown (⊡). Insert: absorbance at 400 nm *versus* pH.

## CONCLUSIONS

the anion used. These odd-valent ions might be complexed (*e.g.* $Ag^\circ + Ag^+ \rightarrow Ag_2^+$) and become poor electron donors. The radicals $I_2^-$, $Br_2^-$, $I_2^-$, $Tl^{2+}$, $CO^-$, $\cdot N_2H_3$ and $CO_3^-$, $\cdot NHOH$ were produced, on reaction of the corresponding compounds with OH radicals, but were found not to transfer an electron to MK.

A survey of the oxidation–reduction reactions of a wide range of organic and inorganic free radicals has been covered in this work. Using menaquinone as a typical electron acceptor, these results have indicated the characteristics of the various types of free radicals which do and which do not interact effectively with menaquinone. The efficiency of electron transfer and the rates of electron transfer are considered to be dependent upon both the redox potential of the free radicals and the redox potential of the acceptor. Indeed, it is presumably the difference $\Delta E_0$ which is of importance. Under the experimental conditions (low doses and low concentration of free radicals) used, $> 90\%$ of the $RH\cdot$ and $RH_2\cdot^-$ radicals produced are expected to react with the acceptor, assuming $k_4$ and $k_5$ are $\geq 2 \cdot 10^8$ $M^{-1} \cdot s^{-1}$. The low percentage of electron transfer to menaquinone observed with some radicals could be due to (a) the formation of more than one species (*e.g.* from the reaction of OH radicals with ascorbic acid, ribose and aromatic and heterocyclic compounds), (b) each radical species has a different redox potential; (c) reaction of the radical with menaquinone does not lead to the formation of the semiquinone radical and (d) the $k_4$ and $k_5$ values for electron transfer to MK are very low, $\ll 1 \cdot 10^8$ $M^{-1} \cdot s^{-1}$, and the radicals undergo instead radical–radical reactions.

While the above results have been interpreted as electron transfer reactions, one cannot exclude the possibility that some of these radicals can add to the quinone and produce similar semiquinone radicals. It is interesting to point out that the reaction of a free radical with a quinone could also be used to identify the nature of the free radical produced based on the known efficiency and rate of electron transfer of various functional groups in an α-position to the odd electron.

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